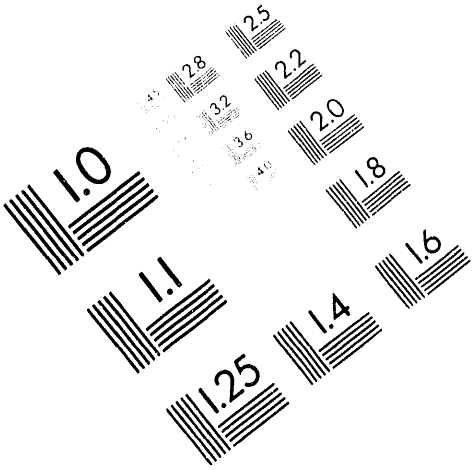

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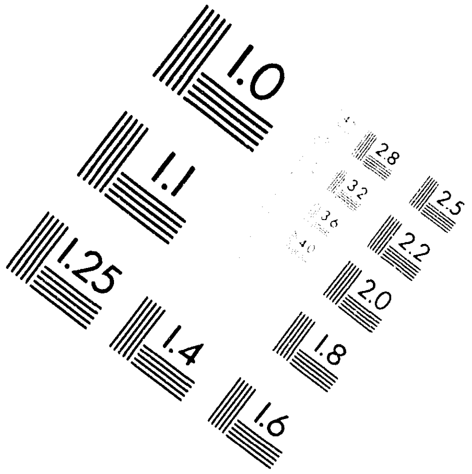

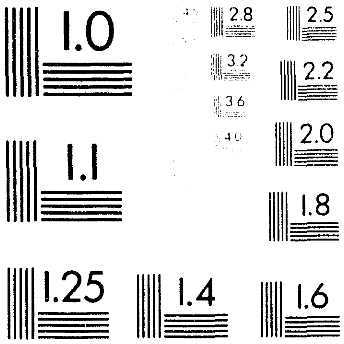

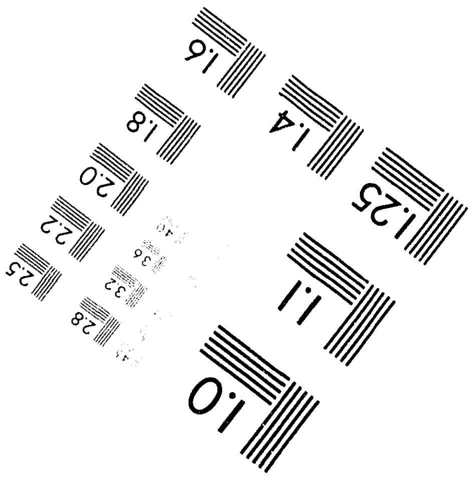

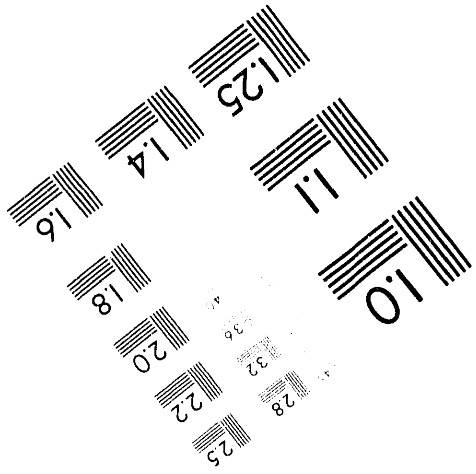

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Title: ANALYSIS OF NEUTRON DIFFRACTION PEAK BROADENING BY INTERNAL STRESSES IN COMPOSITE MATERIALS

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Analysis of Neutron Diffraction Peak Broadening Caused by Internal Stresses in Composite Materials

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Abstract

Neutron diffraction is an essential tool in the study of internal stresses in composite materials. In most work only the peak shifts caused by the related elastic strains are considered, but other valuable information exists in the form of peak shape changes. The conditions under which the pure diffraction profile of the composite (i.e. the profile when all sources of broadening *not* caused by the residual stresses are removed) represents the probability distribution of the peak shifts corresponding to the strains are examined. It is shown that in these conditions, the pure diffraction profile has no attributes of particle size broadening (and *vice versa*), thereby providing a test for the validity of results interpreted in this way. The experimental derivation of measured strain distributions in Al_2O_3/SiC_p composites using neutron diffraction is described. No apparent particle size broadening was detected, demonstrating the validity of the results, which also satisfied other tests for consistency.

1. Introduction

Much effort has been expended on the search for improved structural materials, and one of the most successful approaches has been the development of composite materials, which consist of a mixture of two phases, often with contrasting physical properties. There are many factors which determine the mechanical behaviour of composite materials, but one of the most important is the existence of internal stresses partitioned between the constituent components. These can arise from the thermal expansion mismatch between the components during cooling from processing temperatures, or from their differing mechanical response when the material is stressed. The magnitude of the internal stresses can be very large (several times the macroscopic strength of the composite), and can have either a detrimental or a beneficial effect on the mechanical properties of the material. Either way it is important to measure these stresses, so that the composite can be understood, improved, and used to its maximum potential.

Neutron diffraction is one of the most valuable tools in studying internal stresses in crystalline materials. It can distinguish between the constituent phases of the composite, and in contrast to X-rays and electrons is sufficiently penetrating to see into the bulk of the material, well away from the complicating influence of free surfaces. Its main disadvantage is that its low spatial resolution only allows volumes which are much larger than the distance over which the internal stresses vary to be sampled. In addition, only the average strains, calculated from the shift of the centroids of diffracted peaks, are normally used for subsequent comparison with models for the internal stresses. These are a relatively poor test of models, particularly when it is considered that these frequently contain at least one unknown, such as the amount of relaxation taking place during cooling from processing temperatures [1].

More information is available, however, in the form of broadening of the diffracted peaks (fig. 1), and a number of methods of making use of this has been published. The most rigorous is by Warren and Averbach [2], but the main result to come out of their analysis is the distance over which the internal strains fluctuate. Although this was useful for the problem to which the analysis was applied, namely the nature cold work in metals, it is not very helpful in the study of composite materials, in which it is obvious that the strains fluctuate over a distance corresponding to the spacing between the different microstructural elements. A more useful function to extract would be the measured strain probability distribution function (MSD). Although Warren and Averbach give a rigorous method of extracting the MSD from broadened peaks in principle, it is not practicable, since it requires several orders of the same peak to be fully resolved, and would have a high degree of uncertainty even if this were possible.

It is tempting simply to regard the strain broadened peak as the convolution of the corresponding peak of a suitable strain-free reference specimen with the probability distribution function of the peak shifts corresponding to the measured strains. After all, this would be true if each individual diffracting domain (i. e. grain in the composite) had a uniform strain. Indeed, Warren and Averbach [2] showed that each *column* of atoms normal to the diffracting planes can be considered to contribute separately to the intensity, so this proposition (for brevity called the "probability distribution assumption" below) would also be true if each column had a uniform strain. In addition, Stokes and Wilson [3] have shown that the probability distribution assumption is approximately valid if the strain varies so rapidly that unit cells lose any positional relationship over a distance which is small compared to the size of the diffracting domain. None of these requirements for the probability distribution assumption to hold is generally true for composites, despite which it has sometimes been used in simple, approximate methods which also assume that the form of the MSD is Gaussian [4,5].

This paper describes a practicable but reliable method of extracting the MSD from peak broadening results using the probability distribution assumption. It makes no assumption about the form of the MSD, and incorporates a check on the validity of the probability distribution assumption. The method is illustrated with neutron diffraction results obtained from Al_2O_3/SiC_p composites, which contain large thermal residual stresses owing to the large relaxation-free temperature drop after processing (~1100°C [1]) and the large thermal expansion mismatch ($\Delta\alpha$=3.5 10^{-6}/°C) between the matrix and its reinforcement.

2. Theory

Because each column of atoms normal to the diffracting planes can be considered to make an independent contribution to the total diffracted intensity, only one dimensional crystals need be considered when examining the validity of the probability distribution assumption. Take two co-linear sections of crystal, a extending from x_1 to x_2 with atoms at $nd(1+\varepsilon)$, and b from x_3 to x_4 with atoms at nd, where n is an integer, d is the unstrained lattice parameter, and crystal a has an elastic strain ε relative to the unstrained crystal b. The diffracted intensity distribution in reciprocal space (which becomes the diffraction pattern when sampled by the Ewald sphere) is,

$$FF^* = \frac{\sin^2 \pi u(x_4 - x_3)}{\pi^2 u^2} + \frac{\sin^2 \pi(u+\Delta u)(x_2 - x_1)}{\pi^2 (u+\Delta u)^2}$$
$$+ \frac{2\cos\pi\left[(x_3 + x_4)u - (x_1 + x_2)(u+\Delta u)\right] \sin \pi u(x_4 - x_3) \sin \pi(u+\Delta u)(x_2 - x_1)}{\pi^2 u(u+\Delta u)} \quad (1)$$

where u is the reciprocal coordinate with origin at the centre of the lth order diffraction peak, and $\Delta u = l\varepsilon/d$ is the size of the peak shift caused by a strain ε. The first two terms correspond to the contributions from the two crystals acting independently. The third term is proportional to the product of the square roots of the first two terms, modulated by a cosine function with period inversely proportional to the distance between the centres of the two crystals. The total intensity in the peak and its centroid are given by:

$$\int_{-\infty}^{\infty} FF^* du = (x_4 - x_3) + (x_2 - x_1) \quad (2)$$

and

$$\frac{\int_{-\infty}^{\infty} uFF^* du}{\int_{-\infty}^{\infty} FF^* du} = \frac{-\Delta u(x_2 - x_1)}{(x_4 - x_3) + (x_2 - x_1)} \quad (3)$$

These are the same answers as would have been obtained if the crystals acted independently, there being no contribution from the cross term in eq. 1.

These results can be applied in modelling a 1-D crystal with a slowly varying strain distribution as a string of uniformly strained sections, a, b, c etc. In this case the diffracted intensity is,

$$\begin{aligned} FF^* = \; & F_a F_a^* + F_b F_b^* + F_c F_c^* + \ldots\ldots \\ & + F_a F_b^* + F_a^* F_b \\ & + F_a F_c^* + F_a^* F_c \\ & + \ldots\ldots \end{aligned} \quad (4)$$

Because the cross terms do not contribute to the total intensity and centroid, these quantities are the same as would be found if all the strained sections diffracted independently of one another. They are also the same as the total intensity and centroid predicted by the probability distribution assumption. Thus, although inspection of eqs. 1 and 4 demonstrates that the probability distribution assumption is *not* generally valid for a single column of atoms, if the discrepancy it entails is small compared to the range of differing diffracted peaks scattered from the enormous number of columns present in the gauge volume it can become negligible, as the diffracted energy density in reciprocal space will always be approximately correct. Nevertheless, for practical use, a check on whether or not this "washing out" of the discrepancies has occurred is required, and a simple method of doing so is suggested by the form of eqs. 1 and 4. It can be seen from these equations that one of the main differences between the correct intensity distribution and the prediction of the probability distribution assumption is that the terms representing the individual contributions from the uniformly strained sections of crystal show apparent particle size broadening relative to the width of the peak diffracted from the whole unstrained crystal, i. e. the width implied by the probability distribution assumption. The other major difference arises from the cross terms, and since in general their range is related to the range of the individual contributions from the two sections of crystal from which they originate, they too have some attributes resembling particle size effects. Since particle size broadening is invariant with the order of reflection, l, but the effect of strain is proportional to l a simple experimental test of validity is to compare MSDs calculated using two different orders of the same reflection (or for isotropic cases, two sets of planes with different d spacings). If the same MSD is obtained for both, the result is reliable. If not, the MSD contains a contribution with aspects of particle size broadening, and cannot be used.

3. Summary of Experimental Methods

Composites consisting of Al_2O_3 matrices containing uniform dispersions of SiC particles were prepared by hot pressing mixed powders as has been described previously [1]. SiC powders with average particle sizes of 3μm (microcomposite) and 200nm (nanocomposite) were used, and specimens containing various volume fractions of reinforcement were prepared. Pure Al_2O_3 reference specimens with the same grain size as the composites were also fabricated. The use of solid Al_2O_3 as a reference allows the relatively small intrinsic residual stresses present in this material as a result of its anisotropic thermal expansion to be discounted, and enables the same Al_2O_3 grain size to be used for both the composite and the reference. SiC powders contained in vanadium canisters were used as the corresponding references for the reinforcements.

Neutron diffraction patterns were collected on the HRPD at ISIS and the NPD at LANSCE. Care was taken to make the gauge volumes as similar as possible in size and shape for the references and the composites. For this preliminary work the gauge volumes used were as large as possible and no added collimation was used so that counting statistics were as good as possible. All the results presented are from the backscattered detectors, for maximum resolution.

4. Deconvolution of MSDs from Neutron Diffraction Results

In principle, the pure diffraction peak, $g(t)$, where t is the neutron time of flight, can be calculated as,

$$g = \widehat{\left(\frac{\tilde{h}}{\tilde{f}}\right)} \tag{5}$$

where $h(t)$ is a peak diffracted from the composite and $f(t)$ the corresponding peak from the reference specimen. In practice, however, such direct deconvolution is notoriously susceptible to signal noise, and its application in this case produced nonsensical results. The solution used here was "optimal filtering" [6], the simplest approach to minimizing the effect of noise. In this technique, a mathematical filter is used to weight each frequency component of the function in brackets in eq.5 according to its estimated importance relative to the noise level. The noise level is estimated by inspection of the shape of the power spectral density in reciprocal space, in the present case being modelled as a straight line extrapolated back from the high $1/t$ tail. A summary of the full procedure used follows:

1. Fit and subtract linear background from reference and composite peaks. Normalize results.
2. Create a file containing the optimal filter for the composite peak.
3. Deconvolve to create $g(t)$.
4. Convolve $g(t)$ with $f(t)$ to check that the composite peak is accurately recreated.
5. Divide each value of t in the file containing g by the centroid t of the reference peak and renormalize to obtain the MSD.

5. Results and Discussion

5.1 Deconvolution of the MSD. Fig. 2 shows MSDs obtained for the Al_2O_3 matrices of microcomposites containing 10% and 30% SiC. As is predicted by simple elastic models [1], both MSDs indicate that both positive and negative normal strains were sampled by the neutrons, and that the average strain was positive. The MSD for the higher SiC content is broader and has a higher average strain as expected [1], and the deconvolution process has produced a smooth result. In contrast, the MSD for 10% SiC shows a certain amount of "ringing" in its tails, although this is small enough for the underlying shape to be discernible. This difference in quality of results reflects a general trend which was observed: the deconvolution process is more successful the greater the broadening in the composite peak relative to the reference peak. Thus, not only were better MSDs derived using specimens with a high second phase content, but also the deconvolution process was generally more successful using HRPD/ISIS than with NPD/LANSCE owing to the higher resolution of the former instrument.

In view of this conclusion, two main sources of improvement may be possible for future experiments. First, the experimental setup should be modified to give maximum resolution by using the smallest practical gauge volume and by using extra collimation. This is desirable despite the consequent reduction in count rate, because the noise caused by poorer counting statistics is filtered out to a large extent. In principle higher order reflections give greater strain broadening, although this effect can be negated by instrumental factors. Secondly, fig. 2 suggests that a suitable, careful smoothing of the MSD could remove the ringing without producing misleading results. In any case, it should be borne in mind that the validity of results produced by smoothing can always be monitored by reconvolution with the reference peak.

5.2 Instrumental Effects. If the MSD truly represents a property of the materials only, then the same MSD should be obtained on different instruments. Fig. 3 shows the MSDs for the matrix of the 30% SiC microcomposite derived using the two different diffractometers. Although the NPD result exhibits a small amount of ringing, it is clear that the MSDs are very similar, despite the different gauge volumes used and the different instrumental parameters.

5.3 Influence of Domain Size/Fluctuation Range Ratio. If the probability distribution assumption is valid, all else being equal, the same MSD should be derived when the distance over which the internal stresses fluctuate is much greater than the diffracting domain size as when a number of fluctuations occurs within a single domain. It is difficult to prepare truly comparable materials for this purpose, but the matrix MSDs for microcomposites and nanocomposites provide a good approximation. The former have a grain size similar to the SiC particle size, each reinforcement particle being separated by one or two matrix grains, so each diffracting domain contains one or fewer complete fluctuations of internal stress. In the nanocomposite, the matrix grain size is again a few micrometres, but the 200nm SiC particles are separated by considerably smaller distances than this. Each alumina grain therefore contains a number of SiC particles, and each diffracting domain a corresponding number of fluctuations of the internal stress. Figure 4 shows the matrix MSDs for the 30% SiC micro- and nano-composites. The results were obtained on NPD/LANSCE, so ringing is again apparent in the tails of the MSD, but the agreement between the underlying shapes of the two distributions is close nevertheless, especially when the unavoidable material differences (different SiC particle morphology, differing relaxation-free temperature change etc.) are considered.

5.4 Testing for Apparent Particle Size Broadening. The essential check on the validity of the probability distribution assumption described in section 2 was made by comparing the matrix MSDs for the 30% SiC microcomposite derived from two different Al_2O_3 reflections: {113}, *d*=0.209nm, and {116}, *d*=0.160nm. Although Al_2O_3 is elastically anisotropic, the anisotropy is small compared to the effects caused by the SiC additions, particularly for planes such as these which are at not too dissimilar angles to the principal axes. Different orders of the same reflection which did not overlap with other peaks were not available. Although the 30% difference in *d* spacing between the planes is smaller than would be chosen ideally, the very close agreement between the two MSDs shown in fig.5 demonstrates that there is negligible apparent particle size broadening, and, therefore, that the MSD is a valid description of the normal strains sampled by the neutrons scattered from the gauge volume.

5.5 Implications for Methods of Strain Broadening Analysis Assuming Gaussian MSDs

That there is negligible real or apparent particle size broadening shows that the method of treating strain broadening described here is suitable for the study of discontinuously reinforced ceramic matrix composites. Methods in which the MSD is assumed to be Gaussian, however, frequently produce results which suggest that particle size broadening *is* significant. With this in mind, fig. 6 compares the matrix MSD for the 30% SiC microcomposite with a normalized Gaussian of the same height. The two distributions are sufficiently similar for estimates of the MSD as the Gaussian component of the real MSD to be reasonably accurate. The correspondence is by no means perfect, however. The real MSD is slightly asymmetrical, in the sense predicted by simple elastic models [1], and the discrepancy between the widths of the measured and assumed peaks corresponds to $\delta d/d \approx 4\ 10^{-4}$, which would give very misleading results if erroneously interpreted as particle size broadening. In summary, methods involving the assumption of a Gaussian strain distribution may be suitable for estimating the MSD of materials such as these, but no physical interpretation should be attached to any apparent particle size effects observed, as these are likely to be artefacts of the assumption.

6. Conclusions

1. In some circumstances the pure diffraction peak obtained from material containing an internal stress distribution can be interpreted directly as the probability distribution function of peak shifts corresponding to the normal strains sampled by the neutrons scattered from the gauge volume. This interpretation is valid if and only if experimental results show negligible apparent particle size broadening.

2. Measured strain distributions (MSDs) have been deconvolved from neutron diffraction results obtained from Al_2O_3/SiC_p composites. The results showed negligible apparent particle size broadening, demonstrating their validity, and similar MSDs were extracted using different instruments and different domain size to internal stress range ratios.

3. Simple methods of analysing strain broadening in which the MSD is assumed to be Gaussian provide a good estimate of the actual MSD for materials such as those used here, but apparent particle size effects have little direct physical meaning.

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Figure captions

Fig. 1. {113} Al_2O_3 diffraction peaks for pure Al_2O_3 (solid line) and Al_2O_3/30%SiC microcomposite showing peak broadening.

Fig. 2. MSDs obtained from 10% (solid line) and 30% SiC microcomposites using {113} Al_2O_3 peaks.

Fig. 3. MSDs for the same 30% SiC microcomposite derived using the {113} Al_2O_3 peak on HRPD/ISIS (solid line) and NPD/LANSCE.

Fig. 4. MSDs for 30% SiC nanocomposite (solid line) and microcomposite.{113} Al_2O_3 peak.

Fig. 5. MSDs for the 30% SiC microcomposite matrix, derived from the Al_2O_3 {113} peak (solid line) and the Al_2O_3 {116} peak.

Fig. 6. Comparison of the {113} Al_2O_3 MSD for the 30% SiC microcomposite (solid line) with a normalized Gaussian of the same height.

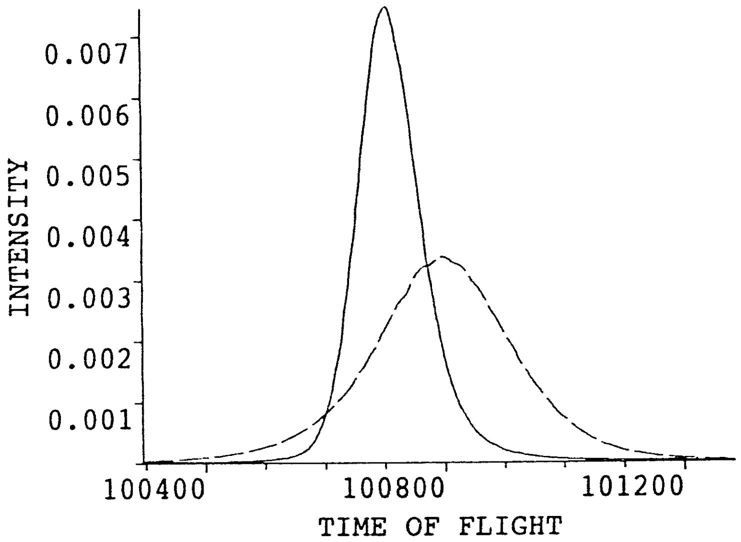
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Fig 1

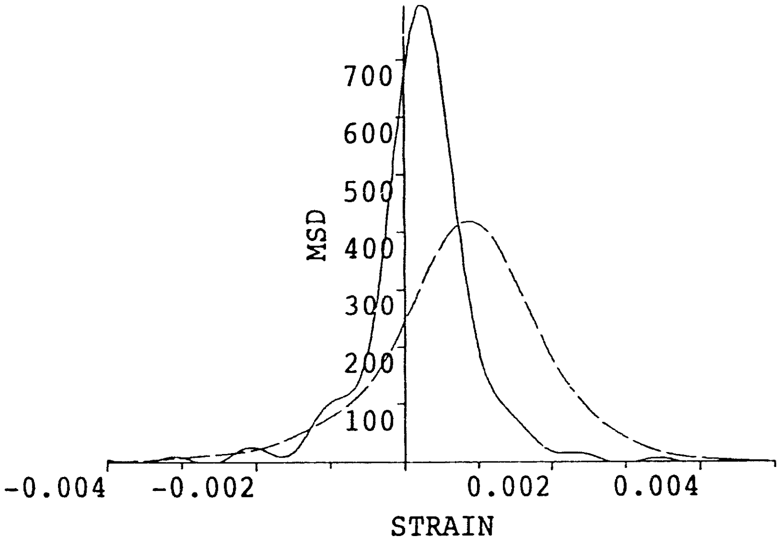

Fig 2

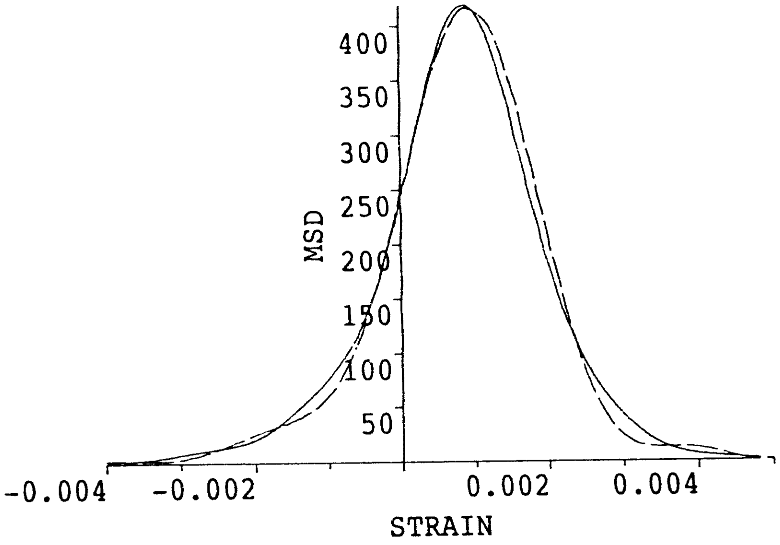

Fig 3

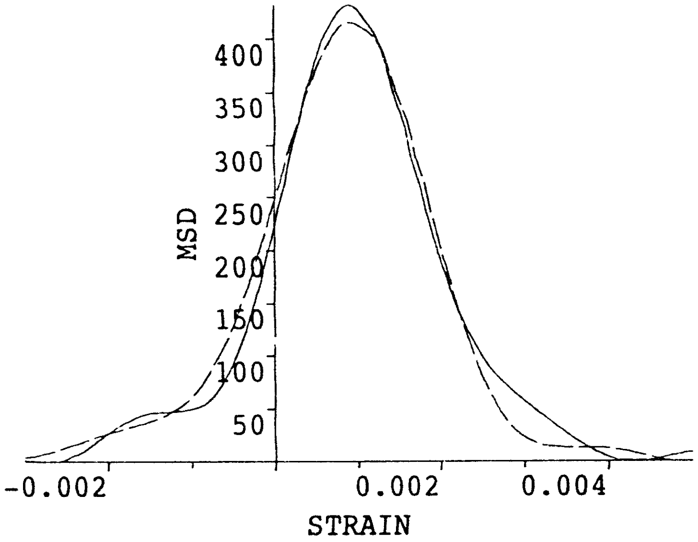

Fig 4

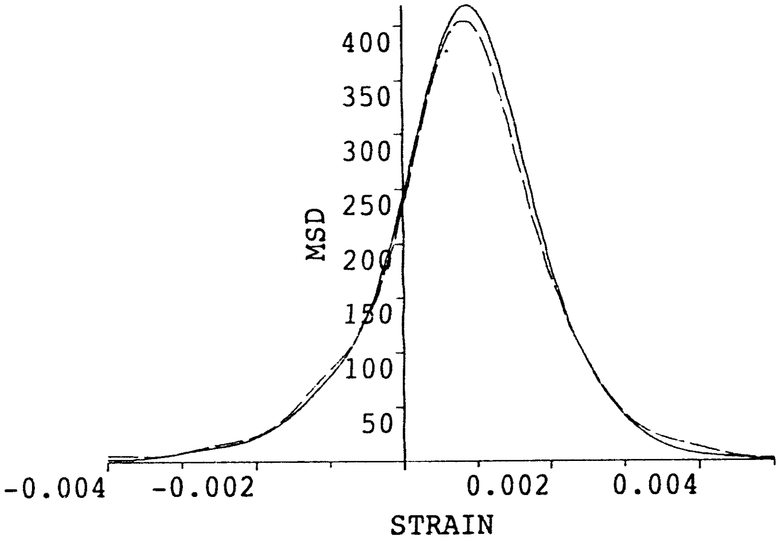

Fig 5

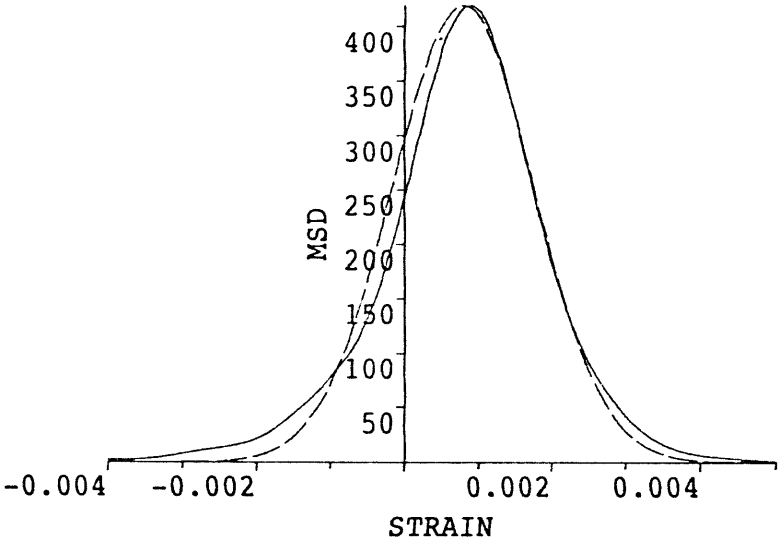

Fig 6

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